

Speed of Sound in Liquid Phase of the Ozone-Safe Refrigerant

Blend R134a–R152a<sup>1</sup>

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## **ABSTRACT**

Speed of sound in the liquid phase of the binary blend of R134A and R152A and its components has been studied. Speed of sound was measured by means of the impulse method at frequency of 2.1 MHz. The temperature range investigated constitutes 230-350K at the pressure up to 16 MPa. The values of speed of sound were measured with standard error of not more than 0.25%.

The results obtained for the both components of the blend are presented with the expressions based on the physical model. The standard deviation of data measured is 0.09%. On a basis of the results obtained the Redlich-Kister correlation has been used within entire intervals of composition, temperature and pressure to determine speed of sound in liquid phase and at the bubble point of the blend investigated.

**KEY WORDS:** equation of state; experimental method; refrigerant; speed of sound; vapour-liquid equilibrium.

## **1. EXPERIMENTAL DATA**

Speed of sound in liquid phase was measured using an impulse method at frequency of 2.1 MHz. The device, which consists of the acoustic cell placed inside the liquid bath and which we described in our previous publications [1] in detail, was examined and tested using water and toluene as the standard samples. The deviation of test data around the standard ones does not exceed 0.07%. The pressure and temperature in the acoustic cell are measured with tensor pressure detector and platinum resistance thermometer, and errors do not exceed 0.1% and 0.02 K respectively. The values of speed of sound in the liquid refrigerants is measured with standard error of no more than 0.25%.

The samples of refrigerant binary solutions were prepared in the laboratory by weighing. The composition of each solution is determined with a standard error of about 0.001 weight fraction.

The experimental data on speed of sound in liquid phase of refrigerant R152A and mixture R134a+R152a, received during the present study at the pressure ranging between saturated curve pressure and up to 20 MPa and temperatures of 220K to 360K, complete our previous study of refrigerants R134A and R152A published in [1-4]. The experimental data obtained are presented in Tables I-IV.

## **3. RESULTS AND DISCUSSION**

### **3.1. Speed of sound**

The data on speed of sound in liquid phase of refrigerant R134A and R152A are generalized in investigated interval by the following polynomial approximation:

$$\omega^3 = \omega_s^3 + \Sigma, \quad (1)$$

$$\Sigma = 10^3 \cdot \sum_{i=0}^2 \sum_{j=1}^3 A_{ij} \tau^i (p - p_s)^j,$$

and the temperature function for speed of sound at the boiling curve ( $\omega_s$ ) is chosen according to [5]:

$$\omega_s = \sum_{i=0}^4 A_i \tau^{n_i}, \quad (2)$$

where  $\tau = 1 - \dot{O}/\dot{O}_c$ , and  $p_s$ ,  $\omega_s$  è  $\dot{O}_c$  are saturated pressure, speed of sound in saturated liquid and critical temperature correspondingly. The parameters of Eqs. (1) and (2) along with standard deviation ( $\sigma$ ) are given in Table V.

For approximation of the data obtained for the mixture R152A+R134A the procedure based on Redlich-Kister correlation was applied. This correlation operates with deflection from the additive value:

$$Y = x_1 x_2 \sum_i^k a_i (x_2 - x_1)^i, \quad (3)$$

$$Y = \Delta \omega = \omega_{mix} - (x_1 \omega_1 + x_2 \omega_2).$$

Speed of sound in mixture at boiling curve is approximated by polynomial expression:

$$\omega_{mix} = \sum_{i=1}^2 x_i \omega_i + x_1 x_2 \sum_{i=0}^2 \sum_{j=0}^2 K_{ij} \tau_{mix}^i (x_2 - x_1)^j, \quad (4)$$

where  $\tau_{mix} = 1 - \dot{O}/\dot{O}_{cmix}$ ,  $\dot{O}_{cmix}$  is critical temperature of mixture which can be defined by formula [6]:

$$T_{cmix} = 386.5 - 7.548 x_1 - 4.722 x_1^2.$$

Speed of sound in liquid phase is supposed to be generalized with following equation:

$$\omega_{\text{mix}} = [\omega_{\text{mix}}^3 + x_1 \Sigma_1 + x_2 \Sigma_2 + x_1 x_2 (p - p'_{\text{mix}}) \sum_{i=0}^1 \sum_{j=0}^1 B_{ij} \tau_{\text{mix}}^i (x_2 - x_1)^j]^{1/3}, \quad (5)$$

where  $\Sigma_1$  and  $\Sigma_2$  are corrections related to the pressure dependence on speed of sound in pure components in Eq. (1).

The constants of Eqs. (3)-(5) found by means of non-linear regression are given in Table VI. The standard deviation is 0.151%, and deviation of experimental data from calculated ones is shown in Fig. 1. The dependence of excess value of speed of sound as regards to additive value at bubble point pressure for different composition of the mixture R134A+R152A is shown in Fig. 2.

### 3.2. Phase equilibrium parameters.

The experimental data [7-9] on the parameters of boiling curve of the investigated mixture were approximated with use of model [10]. For saturation curve parameters of the basic component (R152A) the Wagner correlation [11] was applied. The pressure at the saturation curve of R134A is described with a help of additional coefficients  $\varphi_i$  and  $\theta_i$  incorporated into the same equation. As a result, the saturated vapour pressure values of these refrigerants with standard error of less than 3 kPa are defined by the following equation:

$$\ln(p_i/\varphi_i p_{ci}) = [1/(1 - \tau_i)](A\tau_i^\alpha + B\tau_i^\beta + C\tau_i^\gamma), \quad (6)$$

where  $\tau_i = 1 - T/\theta_i T_{ci}$ ,  $\alpha = 1$ ;  $\beta = 1.5$ ;  $\gamma = 2.5$ ;  $A = -7,469422$ ;  $B = 1.907671$ ;  $C = -2.627579$ .

The critical parameters of the components are:  $T_{c1} = 374.27\text{K}$ ,  $p_{c1} = 4.065 \text{ MPa}$  (for R134A) and  $T_{c2} = 386.41\text{K}$ ,  $p_{c2} = 4.512 \text{ MPa}$  (for R152A). The correlation coefficients  $\varphi_i$

and  $\theta_i$  in accordance with Eq. (6) for R134A are:  $\phi_1=1.33147$  and  $\theta_1=1.04084$ . For R152A these parameters equal 1.

According to the model [10] the boiling pressure data for a mixture ( $p_m$ ) are approximated with the following system of equations:

$$\ln(p_m/p_{cmix}) = [1/(1 - \tau_m)](A\tau_m + B\tau_m^{1.5} + C\tau_m^3), \quad \tau_m = 1 - T/T_{cmix}, \quad (7)$$

$$T_{cmix} = x_1 \theta_1 T_{c1} + \theta_2 T_{c2},$$

$$p_{cmix} = x_1^2 \phi_1 p_{c1} + 2x_1 x_2 (1 - k_{12}) [\phi_1 p_{c1} \phi_2 p_{c2}]^{0.5} + x_2^2 \phi_2 p_{c2},$$

where  $x_1$  and  $x_2$  — mole fraction of the components R134A and R152A. The correlation of  $k_{12}$  coefficient *versus* temperature and composition is used in a form of:

$$k_{12} = k_{12}^0 + k_{12}^1 (T - T_{12}^0) + m_{12} (x_1 - x_2). \quad (8)$$

Here  $k_{12}^0$ ,  $k_{12}^1$ ,  $T_{12}^0$  and  $m_{12}$  are fitting parameters defined by non-linear regression method on a basis of all data measured.

The standard deviation between the experimental boiling curve pressure data and calculated ones is 0.58%, and the parameters of Eqs. (7) and (8) are:  $k_{12}^0 = -0.00270467$ ;  $k_{12}^1 = 0.00007481$ ;  $T_{12}^0 = 95.679$ ; and  $m_{12} = 0.00093333$ .

#### 4. CONCLUSION

Certainly we do not pretend to the completeness of this our report since our study is still continued. A lot of data obtained are still remaining to be processed, e.g. heat capacity, density and *PVT* relation, thermal coefficients, *etc.* Financial support of the Ministry of Industry, Minsk, Belarus, is gratefully acknowledged.

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Table I. Experimental Values of Speed of Sound ( $\omega$ ) in Liquid Phase,  $\text{m}\cdot\text{s}^{-1}$ Refrigerant R152a; ( $T$  in K,  $P$  in MPa)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
302.97	16.23	769.1	271.16	16	902.25	248.53	8	951.42
303.27	.68	622.0	256.73	18.16	913.98	248.53	10	963.42
303.27	1	625.54	256.73	.61	862.88	248.53	12	975.19
303.27	2	636.38	256.73	.79	864.37	248.53	14	986.14
303.27	4	659.1	256.73	1	865.86	248.53	16	996.77
303.27	6	680.62	256.73	2	872.3	233.28	.54	979.06
303.27	8.1	700.94	256.73	4	886.83	233.28	.79	981.25
303.27	10	718.26	256.73	6	900.23	233.28	1	983.72
303.27	12	735.23	256.73	10	925.6	233.28	2	989.82
303.27	14	751.59	256.73	12	938.7	233.28	4	1001.7
303.27	16	767.03	256.73	14	950.38	233.28	6	1012.9
303.27	16.4	769.72	248.53	16	961.3	233.28	8	1024.2
271.16	.55	789.61	248.53	.63	903.47	233.28	10	1036.3
271.16	1	793.89	248.53	.79	905.8	233.28	12	1046.8
271.16	6	832.02	248.53	1	907.2	233.28	14	1055.9
271.16	8	847.45	248.53	2	912.86	233.28	16	1067.1
271.16	10	861.57	248.53	4	926.82			
271.16	12	875.3	248.53	6	938.21			

Table II. Experimental Values of Speed of Sound ( $\omega$ ) in liquid phase,  $\text{m}\cdot\text{s}^{-1}$ R134a + R152a; (0.128 mol. R134a;  $T$  in K,  $P$  in MPa)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
234.15	.499	939.3	270.3	1	766	315.92	8	619.9
234.15	.762	940.8	270.3	2	774.5	315.92	10	640.2
234.15	1	942.3	270.3	4	790.3	315.92	12	659.2
234.15	2	948.5	270.3	6	805.9	315.92	14	675.2
234.15	4	960.1	270.3	8	820.4	315.92	16	693
234.15	6	971.8	270.3	10	833.4	327.58	1.54	479.5
234.15	8	982.4	270.3	12	846.6	327.58	2	487.2
234.15	10	993.3	270.3	14	859.1	327.58	4	518.1
234.15	12	1002.9	270.3	16	871.2	327.58	6	544.1
248.6	.503	869.1	295.71	.759	637.5	327.58	8	569.1
248.6	.762	869.5	295.71	1	640	327.58	10	590.5
248.6	1	872.1	295.71	2	650.1	327.58	12	611
248.6	2	878.4	295.71	4	670.3	327.58	14	630.7
248.6	4	891.8	295.71	6	689.4	327.58	16	650.4
248.6	6	904.9	295.71	8	707.2	336.2	1.72	432.1
248.6	8	916.7	295.71	10	724	336.2	2	437.6
248.6	10	928.3	295.71	12	740	336.2	4	472.7

Table II. (Continued)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
248.6	12	940.5	295.71	14	755.4	336.2	6	503.7
248.6	14	951.5	295.71	16	769	336.2	8	530.9
248.6	16	962.1	306.27	.759	583.6	336.2	10	555.3
256.87	.609	828	306.27	1	586.2	336.2	12	578.3
256.87	.762	829.1	306.27	2	597.4	336.2	14	598.9
256.87	1	830.7	306.27	4	621.1	336.2	16	618
256.87	2	838.4	306.27	6	641.9	350.37	2.56	361.6
256.87	4	852.4	306.27	8	661.4	350.37	3.17	376.6
256.87	6	866.5	306.27	10	679.9	350.37	4	396.5
256.87	8	878.9	306.27	12	697	350.37	6	435.9
256.87	10	891.6	306.27	14	713.8	350.37	8.1	470.7
256.87	12	903.7	306.27	16	728.5	350.37	10	498.3
256.87	14	915.3	315.92	1.361	540	350.37	12	522.7
256.87	16	926.4	315.92	2	548.4	350.37	14	546.9
270.3	.698	763.9	315.92	4	574.9			
270.3	.762	764.4	315.92	6	598.2			

Table III. Experimental Values of Speed of Sound ( $\omega$ ) in Liquid Phase,  $\text{m}\cdot\text{s}^{-1}$ R134a + R152a (0.315 mol. R134a;  $T$  in K,  $P$  in MPa)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
287.01	2.61	663.9	256.86	4	816.8	327.59	14	599.4
287.01	2.86	666.9	256.86	6	830.1	327.59	16	617.8
287.01	4	677.2	256.86	8	843.7	327.59	16.15	618.9
287.01	6	693.8	256.86	10	855	306.24	.878	549.7
287.01	8	709.3	256.86	12	867.9	306.24	1	550.9
287.01	10	725.4	256.86	14	879.8	306.24	2	563.2
287.01	12	741	256.86	16	890.1	306.24	4	586.3
287.01	14	755.6	256.86	16.28	892.3	306.24	6	607
287.01	16	768.8	271.39	.485	720.4	306.24	8	627.4
287.01	16.27	770.7	271.39	.5	720.9	306.24	10	645.8
233.92	.456	899.9	271.39	1	724.7	306.24	12	663.1
233.92	.5	900.4	271.39	2	732.7	306.24	14	679.4
233.92	1	902.4	271.39	4	749.1	306.24	16	693.9
233.92	2	910.9	271.39	6	764.9	315.86	1.027	501.6
233.92	4	923.3	271.39	8	779.2	315.86	1.208	504.1
233.92	6	933.6	271.39	10	793.4	315.86	2	515.2
233.92	8	943.4	271.39	12	806.1	315.86	4	541.6

Table III. (Continued)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
233.92	10	954.2	271.39	14	819.3	315.86	6	565.6
233.92	12	964.7	271.39	16	831.5	315.86	8	586.9
233.92	14	974	271.39	16.23	832.7	315.86	10	607.3
233.92	16	983.6	295.74	.589	598.2	315.86	16	659.9
233.92	16.37	985.8	295.74	.795	600.6	336.19	2	404.7
248.53	.512	830.1	295.74	1	603.3	336.19	4	441.5
248.53	.8	831.7	295.74	4	634.5	336.19	6	473.3
248.53	1	833.5	295.74	8	671.5	336.19	8	499.5
248.53	2	840.4	295.74	10	688.1	336.19	10	525.3
248.53	4	853.1	295.74	12	703.5	336.19	12	547.6
248.53	6	865.7	295.74	16	733	336.19	14	568.6
248.53	8	878.9	295.74	16.11	733.7	336.19	16	587.6
248.53	10	891.2	327.59	1.415	443.6	350.36	2.28	321.6
248.53	12	900.5	327.59	1.62	447.7	350.36	2.65	332
248.53	14	911.8	327.59	1.83	451.2	350.36	4	366.3
248.53	16	921.8	327.59	2	453.9	350.36	6	407.4
248.53	16.26	923	327.59	4	484.1	350.36	8	440.5

Table III. (Continued)

256.86	.492	791.1	327.59	6	511.7	350.36	10	469.7
256.86	.5	791.4	327.59	8	536.6	350.36	12	495.2
256.86	1	795.6	327.59	10	559.5			
256.86	2	802.3	327.59	12	580.5			

Table IV. Experimental Values of Speed of Sound ( $\omega$ ) in Liquid Phase,  $\text{m}\cdot\text{s}^{-1}$ R134a+R152a (0.688 mol. R134a;  $T$  in K,  $P$  in MPa)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
230.23	.687	865.92	272.78	6	705.48	295.67	14	670.96
230.23	.799	866.34	272.78	8	720.07	295.67	16	684.55
230.23	1	867.63	272.78	10	734.05	306.3	1.7	512.03
230.23	2	873.24	272.78	12	747.31	306.3	1.84	513.58
230.23	4	884.45	272.78	14	760.06	306.3	2	515.3
230.23	6	892.32	272.78	16	771.91	306.3	4	538.34
230.23	8	903.11	272.78	16.34	773.61	306.3	6	559.46
230.23	10	913.45	272.78	16.49	774.1	306.3	8	578.99
230.23	12	923.54	288.83	.772	588.6	306.3	10	596.7
230.23	14	932.62	288.83	.882	589.49	306.3	12	613.61
230.23	16	941.36	288.83	1	590.87	306.3	13.83	628.83
230.23	16.27	942.9	288.83	2	600.45	306.3	16	645.17
243.19	.646	803.11	288.83	4	618.93	306.3	16.42	648
243.19	.799	804.03	288.83	4	616.21	315.77	1.62	463.5
243.19	1	805.32	288.83	6	633.48	315.77	2	468.82
243.19	2	811.27	288.83	8.39	653.3	315.77	4	493.78

Table IV. (Continued)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
243.19	4	822.67	288.83	10.21	666.31	315.77	6	517.07
243.19	6	835.98	288.83	13.83	693.66	315.77	8	539.29
243.19	8	847.47	288.83	16	708.2	315.77	10.3	562.55
243.19	10	859.28	288.83	12	680.88	315.77	12.2	579.03
243.19	12	869.71	295.68	.794	552.78	315.77	14.23	596.34
243.19	14	880.17	295.68	.877	553.73	327.59	1.416	398.31
243.19	16	889.76	295.68	1	555.11	327.59	1.62	401.96
243.19	16.08	890.2	295.68	2	565.82	327.59	2	408.24
253.16	.568	755.04	295.68	4	585.22	327.59	8	492.48
253.16	.634	755.69	295.68	6	604.25	327.59	10	515.42
253.16	1	758.62	295.68	8	621.93	327.59	13.28	547.85
253.16	2	765.06	295.68	10	637.8	327.59	16	571.74
253.16	4	778.97	295.68	12	653.9	327.59	16.05	571.74
253.16	6	791.6	295.68	13.83	667.93	336.24	2.17	363.66
253.16	8	803.36	295.68	16	682.58	336.24	2.45	368.83
253.16	10	815.48	295.67	.607	552.01	336.24	2.86	377.13
253.16	12	826.6	295.67	1	556.16	336.24	4	398.43

Table IV. (Continued)

$T$	$P$	$\omega$	$T$	$P$	$\omega$	$T$	$P$	$\omega$
253.16	14	838.23	295.67	1.21	558.17	336.24	6	429.8
253.16	16	848.56	295.67	2	566.27	336.24	8	457.87
253.16	16.5	851.2	295.67	4	586.67	336.24	10	482.49
272.78	.799	664.56	295.67	6	605.59	336.24	12	504.19
272.78	1	666.33	295.67	8	623.13	336.24	13.83	522.81
272.78	2	674.76	295.67	10	640.1	336.24	16	542.69
272.78	4	690.12	295.67	12	655.83	336.24	16.03	543

Table V. Constants of Eqs. (1) and (2)

		<b>R152a</b> $T_C = 386.41$ K; $\sigma = 0.17\%$			
<i>i</i>	<i>n<sub>i</sub></i>	<i>A<sub>i</sub></i>	<i>A<sub>ij</sub></i>		
			<i>j=1</i>	<i>j=2</i>	<i>j=3</i>
0	0.056	71.1291	9375,02	-37,74913	-
1	0.515	81.1976	21354,38	58,6882	-
2	1.0	854.085	88,29415	0,861092	-
3	1.5	2928.56	-	-	-
4	0.621	1170.023	-	-	-
5	1.242	-2737.83	-	-	-

  

		<b>R134a</b> $T_C = 374.27$ K; $\sigma = 0.120\%$			
<i>i</i>	<i>n<sub>i</sub></i>	<i>A<sub>i</sub></i>	<i>A<sub>ij</sub></i>		
			<i>j=1</i>	<i>j=2</i>	<i>j=3</i>
0	0.056	130.6534	5412.091	-3.421151	0.377037
1	0.515	-344.8112	16378.544	34.6088	-2.47812
2	1.0	901.53	-215.971	-238.224	-
3	1.5	282.921	-	-	-
4	0.621	890.269	-	-	-

Table VI. Coefficients  $K_{ij}$  and  $B_{ij}$ 

$i$	$K_{ij}$			$B_{ij}$	
	$j$			$j$	
	0	1	2	0	1
0	-51.13882	-35.81273	-6.371193	-1661300	-1225419
1	-201.41905	192.075775	1186.0470	-5534388	-
2	387.942108	-622.57489	-3519.406	-	-

## **FIGURE CAPTIONS**

Fig. 1. Deviation of data on speed of sound in mixture R134A+R152A from calculated values *versus* mole fraction of R134A and temperature

Fig. 2. Dependence of excess speed of sounds on mole fraction R134A at 240K and 340K for mixture R134A+R152A at bubble point



